



TITLE:

Theoretical study of electronic and solvent reorganization associated with a charging process of organic compounds. I. Molecular and atomic level description of solvent reorganization

AUTHOR(S):

Sato, H; Kobori, Y; Tero-Kubota, S; Hirata, F

CITATION:

Sato, H ...[et al]. Theoretical study of electronic and solvent reorganization associated with a charging process of organic compounds. I. Molecular and atomic level description of solvent reorganization. JOURNAL OF CHEMICAL PHYSICS 2003, 119(5): 2753-2760

ISSUE DATE:

2003-08-01

URL:

<http://hdl.handle.net/2433/39752>

RIGHT:

Copyright 2003 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.

Theoretical study of electronic and solvent reorganization associated with a charging process of organic compounds. I. Molecular and atomic level description of solvent reorganization

Hirofumi Sato^{a)}

Department of Theoretical Studies, Institute for Molecular Science and School of Mathematical and Physical Science, The Graduate University for Advanced Studies, Okazaki 444-8585, Japan

Yasuhiro Kobori and Shozo Tero-Kubota

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Aobaku, Sendai, 980-8577, Japan

Fumio Hirata

Department of Theoretical Studies, Institute for Molecular Science and School of Mathematical and Physical Science, The Graduate University for Advanced Studies, Okazaki 444-8585, Japan

(Received 9 May 2002; accepted 2 May 2003)

The electronic and solvation structures of *N,N*-dimethylaniline in acetonitrile are examined by means of the *ab initio* reference interaction site model self-consistent-field theory coupled with the method to evaluate nonequilibrium solvation free energy developed by Chong *et al.* [J. Phys. Chem. **99**, 10 526 (1995)]. The key quantities characterizing the solvation process—the free-energy profile governing the solvent fluctuations and solvent reorganization—are evaluated from first principles. A new scheme, which enables us to partition solvent reorganization into atomic contributions in the solute molecule, is proposed and used to analyze the process at the atomic level. We found that the linear response approximation holds well and the overall observable λ_s is not much affected by solute geometry, while the individual atomic contribution is significantly changed, especially by the wagging motion of the amino group. © 2003 American Institute of Physics.
[DOI: 10.1063/1.1586257]

I. INTRODUCTION

It is well regarded that solvent reorganization plays an essential role in understanding charge-transfer processes in solution, and its energy λ_s gives a measure of how significant the solvent fluctuation is along the processes. Recently, Kobori *et al.* developed a new experimental technique, which enables one to determine λ_s of a radical pair, based on the time-resolved electron paramagnetic resonance (TR-EPR).¹ Among various ways of estimating λ_s experimentally, a characteristic of the TR-EPR method is that it can estimate λ_s of the radical pair separated in approximately 1.0 nm by using the stochastic-Liouville equation analysis. The TR-EPR method has been applied to a variety of solute–solvent systems, and it has been successful in exploring solute–solvent interactions in molecular detail.

The observed λ_s is regarded to consist of contributions from three different sources: solvent reorganization around donor ($\lambda_{s,D}$), that around the acceptor ($\lambda_{s,A}$), and their interactions ($\lambda_{s,I}$):

$$\lambda_s = \lambda_{s,D} + \lambda_{s,A} + \lambda_{s,I}. \quad (1)$$

Note that only the last term depends on the relative position of donor and acceptor. The first two terms are the solvent reorganization energy associated with the inherent solvation

property of each solute molecule. The approximate expression in the Marcus picture (λ_s^{CMD}), in which the solvent reorganization energies are derived from the Born model, is given by

$$\lambda_s^{CMD}(R) = \frac{1}{2} \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon} \right) \left(\frac{1}{d_D} + \frac{1}{d_A} - \frac{2}{R} \right), \quad (2)$$

where d_D and d_A are radii of the donor and acceptor, and R is distance between them. It is possible in a reasonable way to extract detailed information on the solvent reorganization processes around the individual molecules from the TR-EPR experiment, since the distance R is thought to be fixed around 1.0 nm in the experimental data: therefore, the contribution from the (last) cross term can be regarded as a small constant value. This raises, at the same time, new questions: How are electronic and geometrical structures of the solute related to observed λ_s ? How appropriate is the macroscopic Marcus picture to describe λ_s at the molecular level? Do atoms in a solute molecule evenly contribute to λ_s or not? The same questions should be applied to $\lambda_{s,D}$ or $\lambda_{s,A}$. To answer these questions, we carried out a computation of solvent reorganization energy associated with charging process of a molecule [$\lambda_{s,D}$ in Eq. (1)], which can be regarded as a partial contribution to observed λ_s , and we examined the validity of linear response theory concerning the solvation process from first principles.

Numerous theoretical methods to describe the solvent reorganization processes are reported.^{2,3} Most popular

^{a)}Present address: Department of Molecular Engineering, Kyoto University, Kyoto, Japan.

among those is to sample the configuration space directly taking the solvent fluctuation as an order parameter.^{4,5} Levy *et al.* proposed an alternative method to evaluate the free-energy profile in solution regarding solvent fluctuations as a Gaussian process.⁶ These studies commonly employ the molecular simulation technique and focus on a monoatomic solute system. To our knowledge, computational determination of reorganization energy for a polyatomic system is very limited, and only a few studies based on molecular simulations have been previously reported.^{3,7} There are essential differences between monoatomic and polyatomic molecular systems. In the latter case, at least two reaction coordinates are necessary to describe the actual processes of solvent reorganization experimentally observed: one is the so-called solvent coordinate that is related to the solvent fluctuation mentioned above through electrostatic interaction between the solute and solvent; the other is the internal degrees of freedom of the solute molecule. It is also very likely that the solvent reorganization is coupled not only with the geometry of the solute, but also with its electronic structure. The reason why only monoatomic solute has been treated in previous studies was because there was no theory available to evaluate the electronic structure of a molecule in solution. To describe the electronic structure of a molecule in solution, we have developed a theory called the reference interaction site model and self-consistent field^{8,9} (RISM-SCF), which hybridizes the *ab initio* molecular orbital (MO) theory and the statistical mechanics for molecular liquids. In a previous article,¹⁰ we proposed a method to evaluate the solvent reorganization energy associated with a charging process of a molecule [$\lambda_{s,C}$ (Ref. 11)] using the RISM-SCF and the procedure developed by Chong *et al.* for evaluating the nonequilibrium solvation free energy.¹² In the present article, we propose a procedure that partitions the solvent reorganization energy into atomic contributions. It is noted that such partitioning is very difficult in the framework of molecular simulations. Using the procedure, the validity of the linear response approximation to treat the solvent reorganization can be examined from the viewpoint of atomic contributions. A charging process of *N,N*-dimethylaniline (DMA) in acetonitrile solvent, a popular system in studies of the charge-transfer reaction, is chosen as a model system.

II. COMPUTATIONAL METHODS

The method used here is a combination of the RISM-SCF theory and Chong's procedure for nonequilibrium solvation. Since details of the method have been reported elsewhere,¹⁰ we make a brief sketch of the method.

In the RISM-SCF theory, the total free energy (\mathcal{A}) including solute and solvent is defined by⁹

$$\mathcal{A} = E_{\text{solute}} + \Delta\mu, \quad (3)$$

where E_{solute} represents the electronic energy of a solute molecule including the nuclear repulsion energy:

$$E_{\text{solute}} = \langle \Psi | \hat{H} | \Psi \rangle \\ = \sum_{i,j} \gamma_{ij} h_{ij} + \frac{1}{2} \sum_{i,j,k,l} \Gamma_{ijkl} (\phi_i \phi_j | \phi_k \phi_l) + \sum_{a>b} \frac{Z_a Z_b}{R_{ab}}. \quad (4)$$

The notations used here have the usual meanings in standard *ab initio* electronic structure theory. $\Delta\mu$ is the excess chemical potential (solvation free energy) (Ref. 13) calculated from the RISM equation with the hypernetted-chain (HNC) closure:^{14,15}

$$\Delta\mu = -\frac{\rho}{\beta} \sum_{\alpha s} \int d\mathbf{r} \left[c_{\alpha s}(r) - \frac{1}{2} h_{\alpha s}^2(r) + \frac{1}{2} h_{\alpha s}(r) c_{\alpha s}(r) \right], \quad (5)$$

where $h_{\alpha s}(r)$ and $c_{\alpha s}(r)$ are the total and direct correlation functions, respectively. \mathcal{A} can be regarded as a functional of these site-density correlation functions between solute and solvent as well as of wave functions ($|\Psi\rangle$) of the solute molecule. By solving these coupled equations, the mutually converged E_{solute} and $\Delta\mu$ give energies in the equilibrium state that include coupling of the solute electron and solvent. \mathcal{A} can thus be rewritten as follows:¹⁶

$$\mathcal{A} = E_{\text{isolate}} + E_{\text{pol}} + \Delta\mu, \quad (6)$$

where E_{isolate} is the electronic energy of an isolated solute molecule,¹⁷ whose wave function ($|\Psi_0\rangle$) can be computed by the standard *ab initio* MO method. The second term E_{pol} represents energy for distortion of the electronic structure in the solute molecule:

$$E_{\text{pol}} = E_{\text{solute}} - E_{\text{isolate}} = \langle \Psi | \hat{H} | \Psi \rangle - \langle \Psi_0 | \hat{H} | \Psi_0 \rangle. \quad (7)$$

This is the scheme of the RISM-SCF method, in which the *ab initio* wave functions of the solute molecule and solvent distribution are treated in a self-consistent manner.

The solvent reorganization energy associated with a charging process is concerned with neutral and cationic forms of a DMA molecule. Let \mathbf{q}^0 and \mathbf{q}^+ denote sets of atomic charges of these species obtained from the RISM-SCF wave functions ($|\Psi\rangle$) of a solvated molecule, respectively:

$$\mathbf{q}^0 = (q_1^0, q_2^0, q_3^0, \dots, q_\alpha^0, \dots, q_N^0), \\ \mathbf{q}^+ = (q_1^+, q_2^+, q_3^+, \dots, q_\alpha^+, \dots, q_N^+), \quad (8)$$

where N is the total number of atoms in DMA. A hypothetical charge distribution, as a function of fraction z , is introduced as follows:

$$\mathbf{q}^z = (1-z)\mathbf{q}^0 + z\mathbf{q}^+. \quad (9)$$

By using the procedure described in the previous paper,¹⁰ the final expression of the free-energy profile around the neutral DMA (ΔF^0) is given by

$$\Delta F^0(z) = \Delta\mu(z) - \Delta\mu(0) - z\mathbf{V}_z \cdot \Delta\mathbf{q}, \quad (10)$$

where

$$\Delta\mathbf{q} = \mathbf{q}^+ - \mathbf{q}^0 \quad (11)$$

and

TABLE I. Lennard-Jones parameters.^a

	σ (Å)	ϵ (kcal mol ⁻¹)
DMA/DMA ⁺		
C _{Me}	3.800	0.170
H _A -H _C	1.000	0.055
C1-C4	3.550	0.070
H2-H4	2.420	0.030
N	3.250	0.170
acetonitrile		
Me	3.775	0.207
C	3.650	0.150
N	3.200	0.170

TABLE II. Total energy and its components.

		Structure I	Structure II
DMA	E_{isolate}^a	-363.82905	-363.81977
	E_{pol}^b	0.23	0.36
	$\Delta\mu^b$	14.33	13.86
DMA ⁺	E_{isolate}^a	-363.58231	-363.59207
	E_{pol}^b	0.86	0.23
	$\Delta\mu^b$	-29.54	-26.50

^aGiven in atomic units.

^bGiven in kcal/mol.

$$(\mathbf{V}_z)_\alpha = \rho \sum_j q_{\text{solvent}}^j \int dr 4\pi r^2 \frac{g_{\alpha j}^z(r)}{r}. \quad (12)$$

Note that electrostatic potential on the solute site \mathbf{V}_z is a function of the fraction z since $g_{\alpha j}^z(r)$ is the pair correlation function (PCF) calculated with the hypothetical charge distribution (\mathbf{q}^z). The solvent reorganization energy associated with the charging of DMA is thus obtained by setting $z = 1$ in Eq. (10):

$$\lambda_{s,C}^0 = \Delta\mu(1) - \Delta\mu(0) - \mathbf{V}_1 \cdot \Delta\mathbf{q}. \quad (13)$$

In a similar manner, that of DAM⁺ ($\lambda_{s,C}^+$, the inverse contribution) is given by

$$\Delta F^+(z) = \Delta\mu(z) - \Delta\mu(1) - (z-1)\mathbf{V}_z \cdot \Delta\mathbf{q},$$

$$\lambda_{s,C}^+ = \Delta\mu(0) - \Delta\mu(1) + \mathbf{V}_0 \cdot \Delta\mathbf{q}. \quad (14)$$

While $\Delta F^0(z)$ and $\Delta F^+(z)$ are functions of z , $\lambda_{s,C}^0$ and $\lambda_{s,C}^+$ can be obtained only from the computational results of the equilibrium systems of DMA and DMA⁺. It should be noted that we can examine whether the solvation process is well described within the linear response regime or not, since the present procedure treats higher-order terms beyond those in the linear response theory.¹² In practice, computation of the electronic-structure distortion (E_{pol}) with hypothetical charge distribution is not feasible. However, the contributions can be neglected in this study since they are small enough (see Table II) in the present system as will be seen later.

The electronic wave functions of solvated DMA and DMA⁺ were computed based on the restricted Hartree-Fock (RHF) and the restricted open-shell Hartree-Fock (ROHF) methods, respectively, with Dunning's (9s,5p)/[3s,2p] basis set with a d polarization function on the carbon and nitrogen atoms.¹⁸ DMA and DMA⁺ are modeled with the all-atom-type interaction including 20 sites,¹⁹ whose Lennard-Jones parameters were taken from the literature²⁰ and are summarized in Table I. The three-point model of acetonitrile²¹ was employed to describe the solvent. All the van der Waals interactions between solute and solvent are determined by means of the standard combination rule. The density of acetonitrile is assumed to be 0.011 39 molecule/Å³ at 298.15 K.

III. RESULTS AND DISCUSSION

A. Characterization of the geometry and electronic structure

The molecular structures considered in the present study are those optimized under the point group symmetry of C_s and C_1 for DMA and of C_{2v} for DMA⁺ in the gas phase. The total energies of these structures both in gas (E_{isolate}) and in solution phases are listed in Table II. The complete geometry optimization of the DMA in the gas phase leads preferentially to a configuration with twisted amino group in the C_1 symmetry group. The structure has essentially the same energy as the C_s structure, and the energy difference between them in the gas phase is less than 0.4 kcal/mol, which is in good accordance with the report by Brouwer and Wilbrandt.²² They have also pointed out that the C_s structure is in good agreement with known experimental structures and can account for the vibrational spectra.²² We thus employ the C_s geometry structure instead of the C_1 geometry in the following computation. As pointed out previously,²² the ground state of DMA⁺ is of B_1 symmetry.

The results for selected parameters of geometry and atomic labels are shown in Fig. 1. The structural data obtained for DMA show reasonable agreement with electron diffraction experiments: the C_{Me}-N bond length (1.45 Å) and the CNC bond angle (115.6°) are quite close to the experimental data (1.46 Å and 116°, respectively) while the computed C₁-N bond length (1.40 Å) is slightly shorter than the experimental value (1.43 ± 0.02 Å). The structure of DMA⁺ is planar and belongs to the C_{2v} point group. A remarkable shortening upon ionization is seen in the C₁-N bond (1.32 Å in DMA⁺), implying an increase of the double-bonding character in C₁-N. All the results stated above strongly suggest that the charging process of DMA (DMA → DMA⁺) is associated not only with an electron redistribution, but also with a change of molecular geometry. Therefore, it is crucial for a thorough analysis of the charging process to consider the solvent response not only to a change in the electronic structure, but also to that in molecular geometry. The analysis will involve a dynamic solvent response to the structural change of the molecule, similar in its spirit to the Kramers theory of the reaction rate. There is another factor to be considered concerning the polarization of solvent molecules which can have a significant effect on the charge-transfer reaction. However, such analyses are certainly out of scope of the present study. Here we consider hypothetical reaction paths in which the structure of DMA is

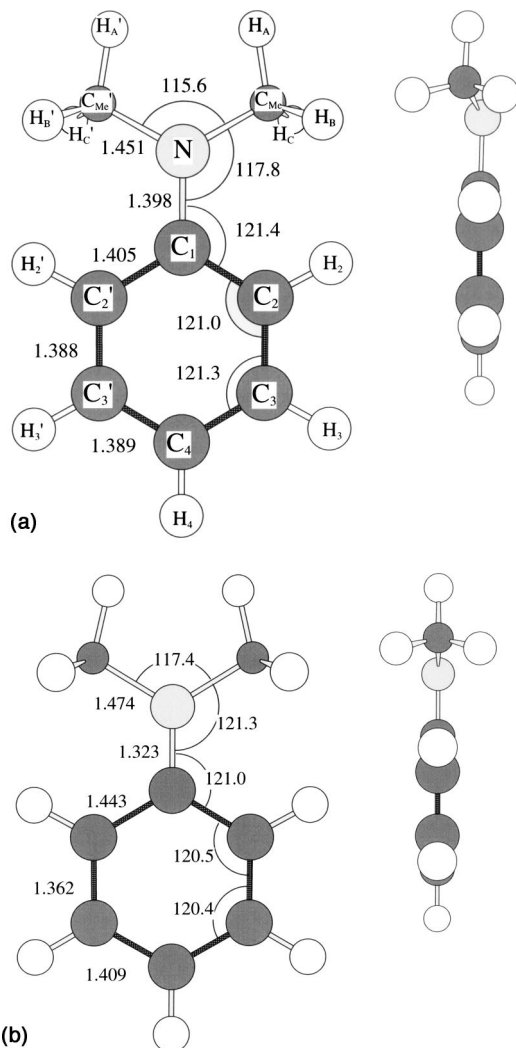


FIG. 1. Selected geometrical parameters and atomic labeling in DMA and DMA⁺: (a) optimized structure under the C_s symmetry of DMA (structure I) and (b) optimized structure under the C_{2v} symmetry of DMA⁺ (structure II).

fixed at one of the two geometries, structures optimized in the gas phase (I and II). Our main focus is put on the electronic structure change in the charging process DMA \rightarrow DMA⁺ and on the solvent reorganization associated with the process.

Figure 2 shows effective charges and their changes upon the charging from DMA to DMA⁺, which are determined by the electrostatic potential (ESP) fitting procedure in acetonitrile solutions. The solid and open squares represent both the direction and magnitude of changes in the effective charges at each atom site indicated in the x axis: the solid and open squares, respectively, symbolize the gain and loss of electrons at the atomic site. The top and bottom edges of the squares correspond to the effective charge in DMA or DMA⁺. Upper and lower panels correspond to the changes of charges in the two structures, structure I and structure II. For example, in the lower panel which corresponds to structure II, electrons are lost at C₂, as indicated by an open square, and the direction of the change is from bottom to top of the square, while electrons are gained at C₃ as shown by a

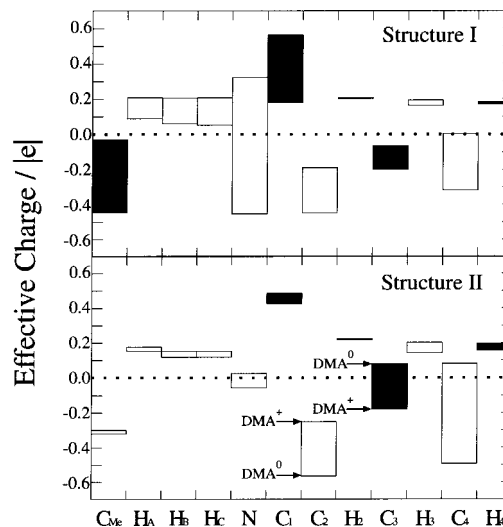
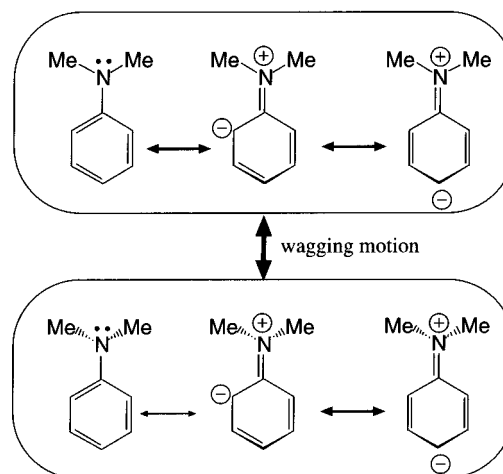


FIG. 2. Effective charges and their changes in the ionization process (DMA \rightarrow DMA⁺). Shaded and nonshaded boxes, respectively, show electron gain and loss, and the top and bottom of boxes indicate effective charge in individual atomic site of DMA and DMA⁺.

solid square, and the effective charge changes from top to bottom. In structure I, the largest (open) square is found in the N site, which means that the most significant change in effective charge (losing electron) occurs at the nitrogen site. Upon the charging process in the structure I, electrons are lost mainly from the N site, although some of electrons are detached from the C₂ and C₄ sites. On the other hand, main changes in the effective charges with respect to structure II take place in the C₂ and C₄ sites. The results can be conveniently, though highly speculatively, interpreted in terms of the resonance structure of DMA. In Scheme 1, the resonance structures of DMA in the structures I and II are depicted.



Scheme 1

It is rather obvious from the resonance structures that the electrons are likely to be accumulated at the C₂ and C₄ sites for both structures I and II, while electrons can be localized also at the N site in case of structure I due to the deviation of the dihedral angle between the planes of the amide and phenyl groups from zero degree or from the planer conformation. Apparently, the deviation of the amide group from the

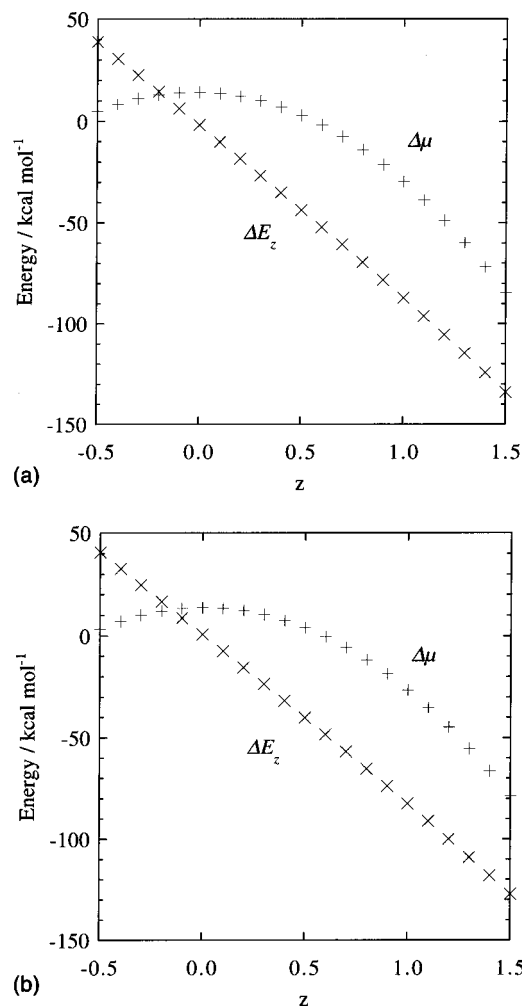


FIG. 3. Dependence of ΔE_z and $\Delta\mu$ on the fraction z : (a) computed at structure **I** and (b) computed at structure **II**.

planar conformation due to the wagging motion partly prevents the lone pair electrons of the N atom from resonance or delocalization. The distributions of effective charges in structures **I** and **II** shown in Fig. 2 are consistent with such a consideration with respect to the resonance structure depicted in scheme 1. As we stated in the preceding paragraph, actual charging processes are determined by changes in the electronic structure and molecular geometry, which are highly coupled, as well as by solvent reorganization which influences both those changes.

B. Solvent fluctuation and its linearity

The reaction coordinate ΔE_z can be calculated as follows:¹²

$$\Delta E_z = \mathbf{V}_z \cdot \Delta \mathbf{q} = \sum_{\alpha} (\mathbf{V}_z)_{\alpha} (\Delta \mathbf{q})_{\alpha}. \quad (15)$$

In Fig. 3, we show ΔE_z as functions of the fraction z for structures **I** and **II**, respectively. Both plottings show straight lines, indicating that the solvation processes are well described in the linear response approximation, although the method employed here is inherently a nonlinear theory. This is in marked contrast to the previous results obtained by the

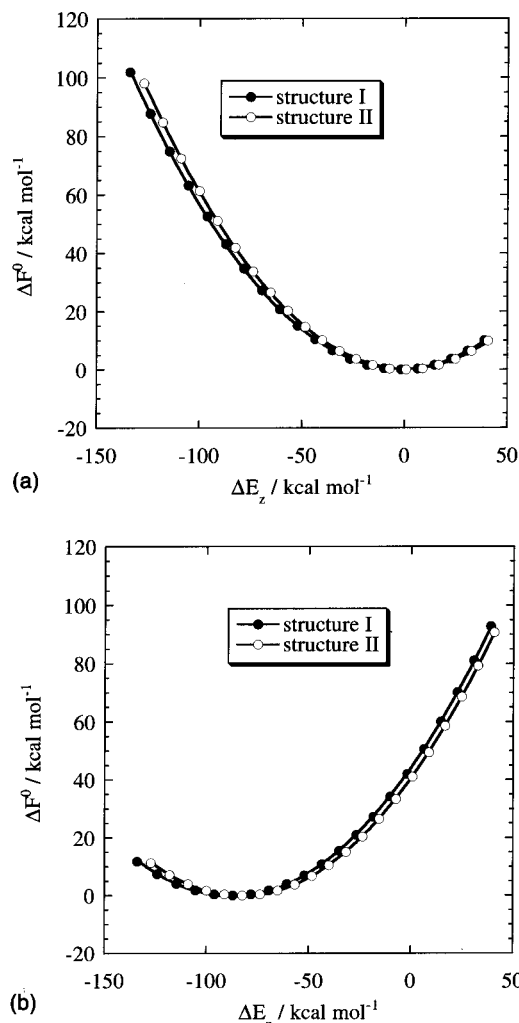


FIG. 4. Free-energy profiles governing the fluctuation ΔE_z of the solvent molecules: (a) around the solute in DMA and (b) around the solute in DMA^+ .

same procedure,¹² in which a simple model system is examined. The reason for the simple behavior in the present study is that the range of electrical potential fluctuations of solvent in the DMA system is quite narrow compared to the previous studies: both equilibrium solvent configurations surrounding neutral and ionized species seem to be in regions close to each other. The results are in good harmony with the conclusion from experimental observation,¹ in which the Marcus model (or linear response approximation) is applicable for several systems.

The free-energy profiles governing fluctuations in ΔE_z are illustrated for DMA and DMA^+ in Fig. 4. The solid lines in the figures correspond to the harmonic approximation obtained by fitting the computed data. The curvatures of the quadratic functions for the two structures **I** and **II** are close

TABLE III. Computed reorganization energy $\lambda_{s,C}$ (eV).

	Structure I	Structure II
DMA	1.88	1.82
DMA^+	1.82	1.78

to each other and show very similar behavior: the force constants (k) in these two structures obtained by the data fitting are 5.83×10^{-3} and $5.99 \times 10^{-3} [\text{kcal/mol}]^{-1}$, respectively. All values of $\lambda_{s,C}$ theoretically obtained from Eqs. (11) and (12) are listed in Table III. The results indicate that the free-energy profiles and $\lambda_{s,C}$ are not strongly affected by geometrical change.

We will not put any stress on the quantitative comparison between results from our theory and the experiment, because our calculations still miss several factors which may or may not affect the final results: for example, contributions from anion species and from the interactions between redox pairs. However, it is worthwhile to make some comparison between the theory and experiment at the “ballpark” level. Since the electronic polarization of solvent is neglected in our present model, it is reasonable to compare with the Born-type approximation of $\lambda_{s,C}^{CMD}$ (Ref. 23):

$$\lambda_{s,C}^{CMD} = \frac{1}{2} \left(1 - \frac{1}{\epsilon} \right) \frac{1}{d_D}, \quad (16)$$

The contribution to $\lambda_{s,C}^{CMD}$ from DMA based on the Eq. (17) can be estimated reasonably with the parameters employed by Kobori *et al.* in the previous study, $\epsilon_s = 37.3$ and $d_D = 3.47 \text{ \AA}$: we get the result $\lambda_{s,C}^{CMD} = 2.0 \text{ eV}$. Our theoretical result, 1.88 or 1.82 eV, shows good agreement with this estimation. Actually, $\lambda_{s,C}^{CMD}$ depends pretty much on the choice of the expression: $\lambda_{s,C}^{CMD}$ based on Eq. (1),

$$\lambda_{s,C}^{CMD} = \frac{1}{2} \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon} \right) \frac{1}{d_D}, \quad (17)$$

with $\epsilon_{op} = 1.8$ leads to a smaller value, 1.10 eV. Such a comparison between the dielectric continuum and the realistic models has been also made in a molecular simulation study.⁷ Ando's estimation for λ_s ranges from 1.7 to 3.3 eV over the distance between a redox pair from 5 to 12 Å. The corresponding experimental λ_s is 1.39 eV measured for DMA-duroquinone in $\text{C}_3\text{H}_7\text{CN}$ solvent.²⁴ It appears that the geometrical change of solute does not affect the solvent reorganization energy λ_s too much for this particular system, since its component $\lambda_{s,C}$ does not change. It suggests that we do not have to be bothered too much in the theoretical study by the structural change of the present DMA system.

C. Partitioning of free-energy profiles into atomic contributions

The solvation free energy, $\Delta\mu$ can “formally” be partitioned into atomic contributions $\Delta\mu_\alpha$ as

$$\Delta\mu = \sum_{\alpha} \Delta\mu_{\alpha}, \quad (18)$$

where “ α ” labels atoms in a solute [see Eq. (5)]. It is noted that $\Delta\mu_\alpha$ is not the same as the solvation energy of an atom α isolated in the solvent, since the total and direct correlation functions of atom α in a solute are perturbed by the existence of the other atoms consisting of the solute. In a similar manner, the contribution from each atomic site to the free-energy profiles governing solvent fluctuations can be defined as follows:

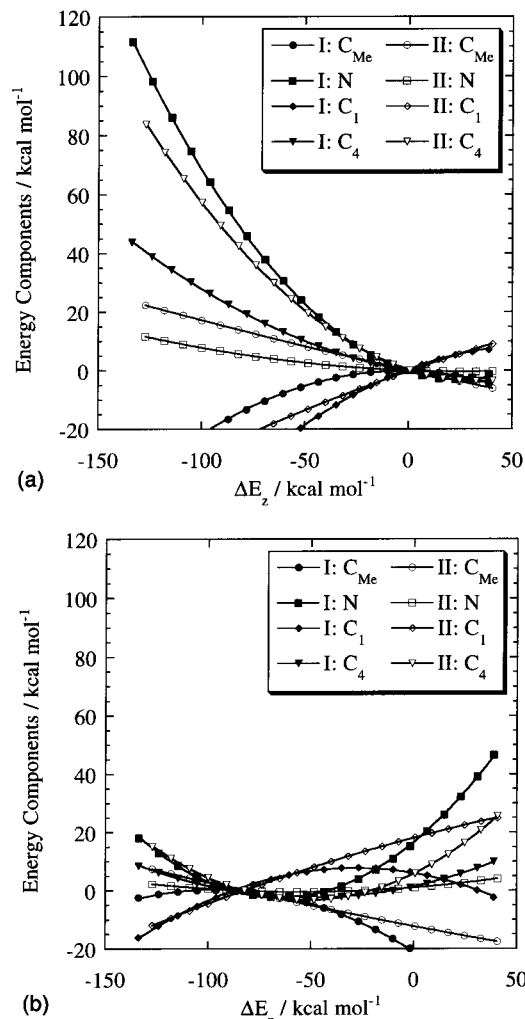


FIG. 5. Components of the free-energy profiles (Δf_α) governing the fluctuation ΔE_z : (a) around the solute in DMA and (b) around the solute in DMA^+ .

$$\Delta F^0 = \sum_{\alpha} \Delta f_{\alpha}^0, \quad \Delta F^+ = \sum_{\alpha} \Delta f_{\alpha}^+ \quad (19)$$

and

$$\begin{aligned} \Delta f_{\alpha}^0(z) &= \Delta\mu_{\alpha}^z - \Delta\mu_{\alpha}^0 - z(\mathbf{V}_z)_{\alpha}(\Delta\mathbf{q})_{\alpha}, \\ \Delta f_{\alpha}^+(z) &= \Delta\mu_{\alpha}^z - \Delta\mu_{\alpha}^1 - (z-1)(\mathbf{V}_z)_{\alpha}(\Delta\mathbf{q})_{\alpha}. \end{aligned} \quad (20)$$

Selected Δf_{α}^0 ($\alpha = \text{N}$, C_4 , and C_{Me} sites) for the two structures (I and II) are plotted together by fitting with quadratic functions (Fig. 5). One may notice that the total free-energy profiles, which are shown in Fig. 4, consist of curves with various curvatures: contributions from the N site and C_4 site are downward convex, while that from the C_1 site is upward convex. All these contributions get together to construct a simple quadratic function.

Another interesting feature seen in the figure is that the contribution from each atomic site depends strongly on the structure of the solute molecule, even though the sum of the contributions is not much changed by the geometrical alteration. All the force constants (k_{α}) regarding individual sites or the second derivative of the free-energy component obtained numerically by fitting the data to quadratic functions

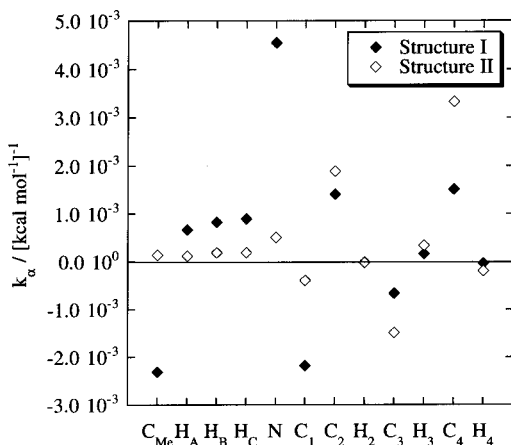


FIG. 6. Distribution of the “force constant” (k_α) assigned to individual atomic sites in DMA/DMA⁺.

are shown in Fig. 6. Here k_α 's for all hydrogen sites are very close to zero, which means that the curves are straight lines rather than quadratic functions. It suggests strongly that hydrogen atoms scarcely participate in the solvent reorganization process. Sites with positively large k_α , such as the N site in structure I and C₂ site and C₄ site in both structures, may be regarded as sites being “well solvated,” since large reorganization energies are required for solvents to fluctuate around these sites. On the other hand, sites with negatively large k_α can be considered to be “poorly solvated.” One can thus understand that the N site in the amino group is well solvated in structure I, while the contribution from the C₄ site is much more important in structure II.

IV. CONCLUSIONS

By using a procedure we have proposed very recently, the solvent reorganization energy $\lambda_{s,C}$ associated with a charging process of organic compounds is evaluated by means of the *ab initio* RISM-SCF method combined with the procedure developed by Chong *et al.* for evaluating the non-equilibrium solvation free energy. By this method, insight into $\lambda_{s,C}$ can be acquired at the molecular level: it is possible to partition $\lambda_{s,C}$ “formally” into contributions from each atom composing the solute molecule. This is the first theoretical study which treats the solvent reorganization around a realistic polyatomic solute taking both the electronic structure and microscopic solvent structure into consideration. The method is applied to the charging process from DMA to DMA⁺, which is related to a direct measurement of λ_s with the modern TR-EPR technique. The theoretical $\lambda_{s,C}$ gives a reasonable account of the experimental λ_s , demonstrating validity of the present method. Although in the present article we have reported a procedure to compute $\lambda_{s,C}$ concerned with individual molecules in the pair, it is straightforward to extend the procedure to compute λ_s or the solvent reorganization energy for a redox pair. It should be emphasized that the present method requires only a set of standard molecular interaction parameters (e.g., OPLS) to solve the RISM equation. The theory is free from any ambiguous pa-

rameters, such as “cavity radius,” which is employed in the theory based on the continuum model in order to adjust the “number” to the experimental results.

Now we answer the questions we asked in the Introduction. We found that the charging process in the present system is well described with linear response theory and that the overall feature of the process does not depend upon the molecular geometry. In other words, the Marcus theory with the parameters adjusted appropriately is a good approximation for the solvent reorganization energy and the overall $\lambda_{s,C}$ is not much altered by the electronic and geometrical structure changes. However, if the solvation processes are partitioned and viewed at the atomic level, they show ample variety: some of them are described with nice harmonic-type functions and some others with linear functions. The motion of the amino group characterizes the detailed feature of the solvation.

In a subsequent article, we will propose another method to explore the solvent reorganization process. It is well regarded that the electrostatic interaction plays a significant role in the solvent fluctuation. On the other hand, the solvation structure is governed not only by the electrostatic contribution, but by repulsive interactions, which must be related to the geometry of molecules. This method can decompose the solvent reorganization energy into these two contributions.

ACKNOWLEDGMENTS

We gratefully acknowledge Dr. Ryo Akiyama (Cornell University) for invaluable discussions. This research was supported by a Grant-in Aid for Scientific Research on Priority Areas “Molecular Physical Chemistry” (No. 403-11166276), Grant-in Aid for Encouragement of Young Scientists, and from the Japanese Ministry of Education, Science, Sports and Culture (MONBU SHO).

- ¹(a) Y. Kobori, T. Yago, K. Akiyama, and S. Tero-Kubota, J. Am. Chem. Soc. **123**, 9722 (2001); (b) Y. Kobori, K. Akiyama, and S. Tero-Kubota, J. Chem. Phys. **113**, 465 (2000); (c) J. Phys. Chem. A **103**, 5416 (1999); (d) Y. Kobori, K. Zikihara, T. Yago, K. Akiyama, H. Sato, F. Hirata, and S. Tero-Kubota (unpublished); (e) T. Yago, Y. Kobori, K. Akiyama, and S. Tero-Kubota, J. Phys. Chem. B **106**, 10 074 (2002).
- ²B. Roux, H.-A. Yu, and M. Karplus, J. Phys. Chem. **94**, 4683 (1990).
- ³J. Åqvist and T. Hansson, J. Phys. Chem. **100**, 9512 (1996).
- ⁴E. A. Carter and J. T. Hynes, J. Phys. Chem. **93**, 2184 (1989); D. A. Zichi, G. Cicciotti, J. T. Hynes, and M. Ferrario, *ibid.* **93**, 6262 (1989).
- ⁵A. Warshel, J. Phys. Chem. **86**, 2218 (1982).
- ⁶R. M. Levy, M. Belhadj, and D. B. Kitchen, J. Chem. Phys. **95**, 3627 (1991).
- ⁷K. Ando, J. Chem. Phys. **101**, 2850 (1994).
- ⁸S. Ten-no, F. Hirata, and S. Kato, J. Chem. Phys. **100**, 7443 (1994).
- ⁹H. Sato, F. Hirata, and S. Kato, J. Chem. Phys. **105**, 1546 (1996).
- ¹⁰H. Sato and F. Hirata, J. Phys. Chem. A **106**, 2300 (2002).
- ¹¹Hereafter, we use λ_C instead of λ_D or λ_A , since the procedure for donors or acceptors is the same.
- ¹²S.-H. Chong, S. Miura, G. Basu, and F. Hirata, J. Phys. Chem. **99**, 10 526 (1995); S.-H. Chong and F. Hirata, Mol. Simul. **16**, 3 (1996); J. Chem. Phys. **106**, 5225 (1997); Chem. Phys. Lett. **293**, 119 (1998); R. Akiyama, M. Kinoshita, and F. Hirata, *ibid.* **305**, 251 (1999).
- ¹³S. J. Singer and D. Chandler, Mol. Phys. **55**, 621 (1985).
- ¹⁴D. Chandler and H. C. Andersen, J. Chem. Phys. **57**, 1930 (1972).
- ¹⁵F. Hirata and P. J. Rossky, Chem. Phys. Lett. **83**, 329 (1981); F. Hirata, B. M. Pettitt, and P. J. Rossky, J. Chem. Phys. **77**, 509 (1982); F. Hirata, P. J. Rossky, and B. M. Pettitt, *ibid.* **78**, 4133 (1983).
- ¹⁶H. Sato and F. Hirata, J. Am. Chem. Soc. **121**, 3460 (1999).

- ¹⁷The electronic polarization energy of the solute (E_{pol}) in this article corresponds to the solute reorganization energy E_{reorg} in our previous studies. We use E_{pol} throughout this article to avoid confusing it with the solvent reorganization (λ_s), as well as to make clear that the nuclear positions of the solute molecule are fixed upon transferring from the gas phase to the acetonitrile solutions.
- ¹⁸S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965); T. H. Dunning, *ibid.* **53**, 2823 (1970).
- ¹⁹We have also examined the 14-site model, in which the aromatic ring is modeled with 6 sites (united C–H atoms) and found it is not proper for the present molecular system. The partial charges derived from the ESP procedure converged to unphysical values.
- ²⁰W. L. Jorgensen, E. R. Laird, T. B. Nguyen, and J. Tirado-Rives, J. Comput. Chem. **14**, 206 (1993).
- ²¹W. L. Jorgensen and J. M. Briggs, Mol. Phys. **63**, 547 (1988).
- ²²A. M. Brouwer and R. Wilbrandt, J. Phys. Chem. **100**, 9678 (1996).
- ²³S. Lee and J. T. Hynes, J. Chem. Phys. **88**, 6853 (1988); H. J. Kim and J. T. Hynes, *ibid.* **93**, 5194 (1990); M. A. Aguilar, F. J. Olivares del Valle, and J. Tomasi, *ibid.* **98**, 7375 (1993).
- ²⁴H. Sato, Y. Kobori, S. Tero-Kubota, and F. Hirata (unpublished).